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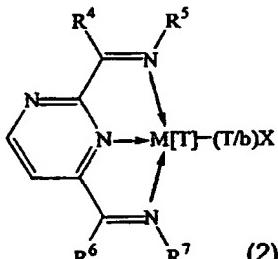
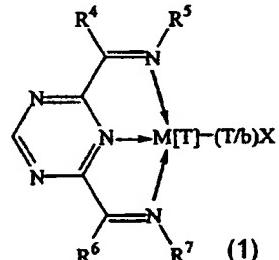
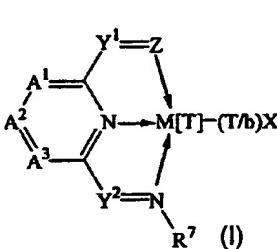
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(54) Title: POLYMERISATION CATALYST



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(57) Abstract: A complex suitable for use as a catalyst in the polymerisation of olefins is disclosed, having the Formula (I) wherein M is a transition metal; X represents an atom or group covalently or ionically bonded to M; T is the oxidation state of M; b is the valency of the atom or group X; A<sup>1</sup> to A<sup>3</sup> are each independently N or P or CR, with the proviso that at least one but no more than two of them are independently CR; Y<sup>1</sup> and Y<sup>2</sup> are each independently CR' or PR'R"; Z is oxygen or NR<sup>5</sup>, R<sup>5</sup> and R<sup>7</sup> and each R, each R' and each R" are independently selected from hydrogen, halogen, hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl, substituted heterohydrocarbyl or SiR<sup>30</sup>, where each R<sup>30</sup> is independently selected from hydrogen, halogen, hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl and substituted heterohydrocarbyl; but excluding those complexes having the formulae (1) and (2) where in both cases R<sup>4</sup> and R<sup>6</sup> are Me, R<sup>5</sup> and R<sup>7</sup> are 2, 4, 6-trimethylphenyl, M is Fe, T is II, X is Cl and b is 1.

### POLYMERISATION CATALYST

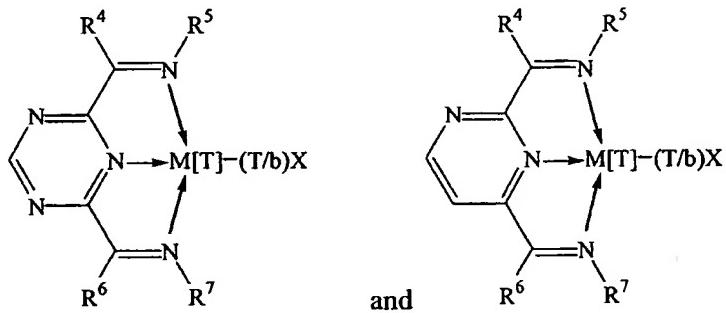
The present invention relates to transition metal complex compounds, to polymerisation catalysts based thereon and to their use in the polymerisation and copolymerisation of olefins.

The use of certain transition metal compounds to polymerise 1-olefins, for example, ethylene or propylene, is well established in the prior art. The use of Ziegler-Natta catalysts, for example, those catalysts produced by activating titanium halides with organometallic compounds such as triethylaluminium, is fundamental to many commercial processes for manufacturing polyolefins. Over the last twenty or thirty years, advances in the technology have led to the development of Ziegler-Natta catalysts which have such high activities that olefin polymers and copolymers containing very low concentrations of residual catalyst can be produced directly in commercial polymerisation processes. The quantities of residual catalyst remaining in the produced polymer are so small as to render unnecessary their separation and removal for most commercial applications. Such processes can be operated by polymerising the monomers in the gas phase, or in solution or in suspension in a liquid hydrocarbon diluent. Polymerisation of the monomers can be carried out in the gas phase (the "gas phase process"), for example by fluidising under polymerisation conditions a bed comprising the target polyolefin powder and particles of the desired catalyst using a fluidising gas stream comprising the gaseous monomer. In the so-called "solution process" the (co)polymerisation is conducted by introducing the monomer into a solution or suspension of the catalyst in a liquid hydrocarbon diluent under conditions of temperature and pressure such that the produced polyolefin forms as a solution in the hydrocarbon diluent. In the "slurry process" the temperature, pressure

and choice of diluent are such that the produced polymer forms as a suspension in the liquid hydrocarbon diluent. These processes are generally operated at relatively low pressures (for example 10-50 bar) and low temperature (for example 50 to 150°C).

In recent years the use of certain metallocene catalysts (for example 5 biscyclopentadienylzirconiumdichloride activated with alumoxane) has provided catalysts with potentially high activity. However, metallocene catalysts of this type suffer from a number of disadvantages, for example, high sensitivity to impurities when used with commercially available monomers, diluents and process gas streams, the need to use large quantities of expensive alumoxanes to achieve high activity, and 10 difficulties in putting the catalyst on to a suitable support.

EP 0924223A discloses a class of catalyst activators, and also provides a long list of catalysts which they may activate. Amongst the catalysts are disclosed two complexes having the formulae



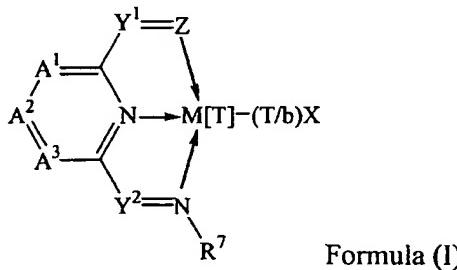
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where in both cases R<sup>4</sup> and R<sup>6</sup> are Me, R<sup>5</sup> and R<sup>7</sup> are 2,4,6-trimethylphenyl, M is Fe, T is II, X is Cl and b is 1. There is no evidence as to whether the compounds were actually made, nor any disclosure as to how the compounds might be made.

An object of the present invention is to provide a novel catalyst suitable for 20 polymerising and oligomerising monomers, for example, olefins such as α-olefins containing from 2 to 20 carbon atoms, and especially for polymerising ethylene alone, propylene alone, or for copolymerising ethylene or propylene with other 1-olefins such as C<sub>2-20</sub> α-olefins. A further object of the invention is to provide an improved process for the polymerisation of olefins, especially of ethylene alone or the copolymerisation 25 of ethylene or propylene with higher 1-olefins to provide homopolymers and copolymers having controllable molecular weights. For example, using the catalysts of the present invention there can be made a wide variety of products such as, for example,

liquid polyolefins, oligomers, linear  $\alpha$ -olefins, branched  $\alpha$ -olefins, resinous or tacky polyolefins, solid polyolefins suitable for making flexible film and solid polyolefins having high stiffness.

The present invention provides a complex having the Formula (I)



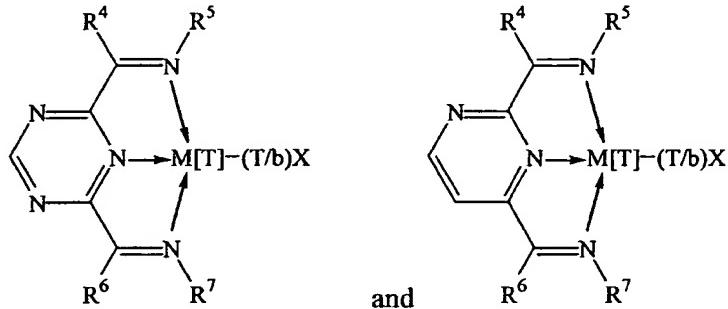
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Formula (I)

wherein M is a transition metal; X represents an atom or group covalently or ionically bonded to M; T is the oxidation state of M; b is the valency of the atom or group X; A<sup>1</sup> to A<sup>3</sup> are each independently N or P or CR, with the proviso that at least one but no more than two of them are independently CR; Y<sup>1</sup> and Y<sup>2</sup> are each

- 10 independently CR' or PR'R''; Z is oxygen or NR<sup>5</sup>; R<sup>5</sup> and R<sup>7</sup> and each R, each R' and each R'' are independently selected from hydrogen, halogen, hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl, substituted heterohydrocarbyl or SiR<sup>30</sup><sub>3</sub> where each R<sup>30</sup> is independently selected from hydrogen, halogen, hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl and substituted heterohydrocarbyl;

- 15 but excluding those complexes having the formulae

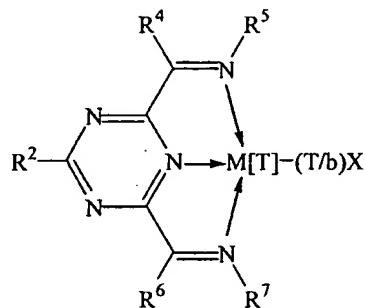


where in both cases R<sup>4</sup> and R<sup>6</sup> are Me, R<sup>5</sup> and R<sup>7</sup> are 2,4,6-trimethylphenyl, M is Fe, T is II, X is Cl and b is 1.

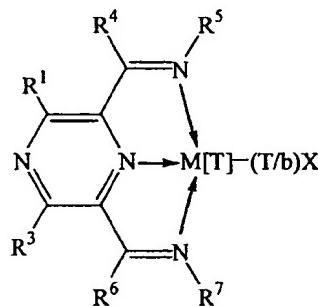
- Preferred are complexes of iron, cobalt, vanadium, titanium, ruthenium, hafnium, 20 manganese, zirconium, rhodium or iridium.

It is preferred that A<sup>1</sup> to A<sup>3</sup> are each independently N or CR, subject to the above proviso. Preferably one or both of A<sup>1</sup> and A<sup>3</sup> are N, or alternatively A<sup>2</sup> alone is N. Preferably Z is NR<sup>5</sup>.

Preferably Y<sup>1</sup> is CR<sup>4</sup> and Y<sup>2</sup> is CR<sup>6</sup>. In one embodiment at least one and 5 preferably both of R<sup>4</sup> and R<sup>6</sup> is a hydrocarbyl group having at least two carbon atoms. Preferably at least one of R<sup>4</sup> and R<sup>6</sup> has from 2 to 12 carbon atoms, and more preferably from 3 to 10 carbon atoms. Preferred such groups for R<sup>4</sup> and R<sup>6</sup> are ethyl, isopropyl, t-butyl, phenyl or CH<sub>2</sub>CH<sub>2</sub>Ph.



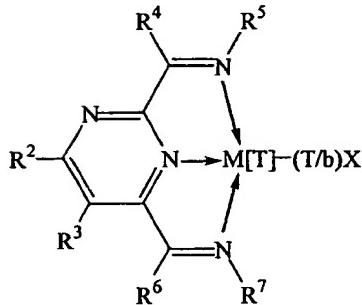
Preferred embodiments include the following:



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Formula (IIa)

Formula (IIb)



Formula (IIc)

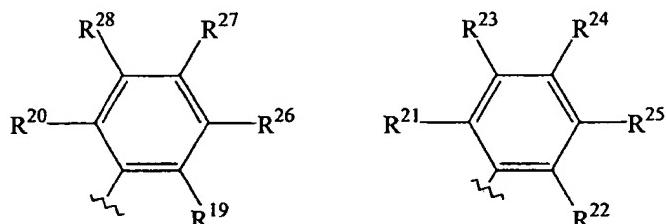
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wherein R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> are each independently H, or C<sub>1</sub>-C<sub>10</sub> alkyl, aryl or arylalkyl, and the other substituents are as defined previously, subject to the above-

mentioned proviso regarding excluded compounds. Preferably R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> are each independently H or C<sub>1</sub>-C<sub>10</sub> alkyl, and more preferably they are each independently H, methyl or ethyl. In formula (IIc), R<sup>2</sup> is preferably methyl.

R<sup>5</sup> and R<sup>7</sup> are preferably independently selected from substituted or unsubstituted 5 alicyclic, heterocyclic or aromatic groups, for example, phenyl, 1-naphthyl, 2-naphthyl, 2-methylphenyl, 2-ethylphenyl, 2,6-diisopropylphenyl, 2,3-diisopropylphenyl, 2,4-diisopropylphenyl, 2,6-di-n-butylphenyl, 2,6-dimethylphenyl, 2,3-dimethylphenyl, 2,4-dimethylphenyl, 2-t-butylphenyl, 2,6-diphenylphenyl, 2,4,6-trimethylphenyl, 2,6-trifluoromethylphenyl, 4-bromo-2,6-dimethylphenyl, 3,5-dichloro2,6-diethylphenyl, 10 and 2,6-bis(2,6-dimethylphenyl)phenyl, cyclohexyl and pyridinyl.

I In a preferred embodiment R<sup>5</sup> is represented by the group "P" and R<sup>7</sup> is represented by the group "Q" as follows:



15                   Group P                   Group Q

wherein R<sup>19</sup> to R<sup>28</sup> are independently selected from hydrogen, halogen, hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl or substituted heterohydrocarbyl; when any two or more of R<sup>1</sup> to R<sup>4</sup>, R<sup>6</sup> and R<sup>19</sup> to R<sup>28</sup> are hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl or substituted heterohydrocarbyl, said two or more can be linked to form one or more cyclic 20 substituents.

The ring systems P and Q are preferably independently 2,6-hydrocarbylphenyl or fused-ring polycyclic, for example, 1-naphthyl, 2-naphthyl, 1-phenanthrenyl and 8-quinolinyl.

25                   Preferably at least one of R<sup>19</sup>, R<sup>20</sup>, R<sup>21</sup> and R<sup>22</sup> is hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl or substituted heterohydrocarbyl. More preferably at least one of R<sup>19</sup> and R<sup>20</sup>, and at least one of R<sup>21</sup> and R<sup>22</sup>, is hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl or substituted heterohydrocarbyl. Most preferably R<sup>19</sup>, R<sup>20</sup>, R<sup>21</sup> and R<sup>22</sup> are all independently selected from hydrocarbyl, substituted

hydrocarbyl, heterohydrocarbyl or substituted heterohydrocarbyl. R<sup>19</sup>, R<sup>20</sup>, R<sup>21</sup> and R<sup>22</sup> are preferably independently selected from methyl, ethyl, n-propyl, iso-propyl, n-butyl, sec-butyl, tert.-butyl, n-pentyl, neopentyl, n-hexyl, 4-methylpentyl, n-octyl, phenyl and benzyl.

5 R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>6</sup>, R<sup>19</sup>, R<sup>20</sup>, R<sup>21</sup>, R<sup>22</sup>, R<sup>23</sup>, R<sup>25</sup>, R<sup>26</sup> and R<sup>28</sup> are preferably independently selected from hydrogen and C<sub>1</sub> to C<sub>8</sub> hydrocarbyl, for example, methyl, ethyl, n-propyl, n-butyl, t-butyl, n-hexyl, n-octyl, phenyl and benzyl.

In one embodiment R<sup>24</sup> and R<sup>27</sup> are either both halogen or at least one of them has two or more carbon atoms.

10 In an alternative embodiment R<sup>5</sup> is a group having the formula -NR<sup>29</sup>R<sup>30</sup> and R<sup>7</sup> is a group having the formula -NR<sup>31</sup>R<sup>32</sup>, wherein R<sup>29</sup> to R<sup>32</sup> are independently selected from hydrogen, halogen, hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl or substituted heterohydrocarbyl; when any two or more of R<sup>1</sup> to R<sup>4</sup>, R<sup>6</sup> and R<sup>29</sup> to R<sup>32</sup> are hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl or substituted heterohydrocarbyl, said two or more can be linked to form one or more cyclic substituents.

The atom or group represented by X in the compounds of Formula (I) can be, for example, selected from halide, sulphate, nitrate, thiolate, thiocarboxylate, BF<sub>4</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup>, hydride, hydrocarbyloxide, carboxylate, hydrocarbyl, substituted hydrocarbyl and heterohydrocarbyl, or β-diketonates. Examples of such atoms or groups are chloride, bromide, methyl, ethyl, propyl, butyl, octyl, decyl, phenyl, benzyl, methoxide, ethoxide, isopropoxide, tosylate, triflate, formate, acetate, phenoxide and benzoate. Preferred examples of the atom or group X in the compounds of Formula (I) are halide, for example, chloride, bromide; hydride; hydrocarbyloxide, for example, methoxide, ethoxide, isopropoxide, phenoxide; carboxylate, for example, formate, acetate, benzoate; hydrocarbyl, for example, methyl, ethyl, propyl, butyl, octyl, decyl, phenyl, benzyl; substituted hydrocarbyl; heterohydrocarbyl; tosylate; and triflate. Preferably X is selected from halide, hydride and hydrocarbyl. Chloride is particularly preferred.

Examples of complexes of the present invention include  
 30 2,4-{[N-(2,6-dimethylphenyl)]phenylimidoyl}6-methyl pyrimidine iron (II)  
 dichloride  
 2,4-{[N-(2,4,6-trimethylphenyl)]phenylimidoyl}6-methyl pyrimidine iron (II)

dichloride

2,4-{[N-(2,6-dimethyl-4-*tert*butylphenyl)]phenylimidoyl}6-methyl pyrimidine

iron (II) dichloride

2,4-{[N-(2-methylphenyl)]phenylimidoyl}6-methyl pyrimidine iron (II) dichloride

5 2,4-{[N-(1,1-diphenylamino)]phenylimidoyl}6-methyl pyrimidine iron (II)  
dichloride

2,6-{[N-(2,6-dimethylphenyl)]phenylimidoyl} pyrazine iron (II) dichloride

2,6-{[N-(2,4,6-trimethylphenyl)]phenylimidoyl} pyrazine iron (II) dichloride

2,6-{[N-(2,6-dimethyl-4-*tert*butylphenyl)]phenylimidoyl} pyrazine iron (II)

10 dichloride

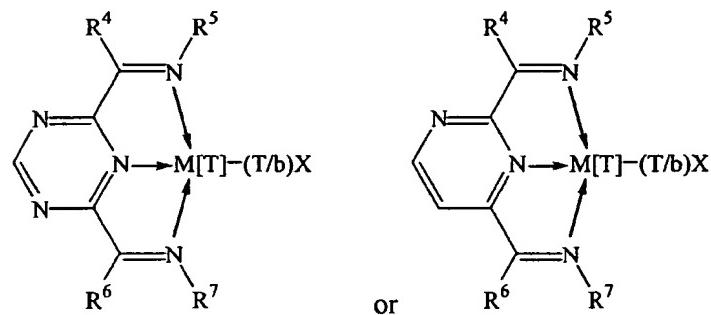
2,6-{[N-(2-methylphenyl)]phenylimidoyl} pyrazine iron (II) dichloride.

The present invention further provides a polymerisation catalyst comprising

(1) a complex of the formula (I) above, and

(2) an activating quantity of at least one activator compound,

15 but excluding the case where compound (1) is



where in both cases R<sup>4</sup> and R<sup>6</sup> are Me, R<sup>5</sup> and R<sup>7</sup> are 2,4,6-trimethylphenyl, M is

20 Fe, T is II, X is Cl and b is 1,

and the activator (2) is a compound obtainable by reacting:

i) a compound comprising a metal of Group 13 of the Periodic Table;

ii) a compound capable of reacting with that of i) to be bonded to two or more of the Group 13 metal;

25 iii) a compound capable of reacting with that of i) to form an ionising ionic compound.

The activator compound for the catalyst of the present invention is suitably selected from organoaluminium compounds and hydrocarbylboron compounds. Suitable organoaluminium compounds include compounds of the formula  $\text{AlR}_3$ , where each R is independently  $\text{C}_1\text{-C}_{12}$  alkyl or halo. Examples include trimethylaluminium (TMA), triethylaluminium (TEA), tri-isobutylaluminium (TIBA), tri-n-octylaluminium, methylaluminium dichloride, ethylaluminium dichloride, dimethylaluminium chloride, diethylaluminium chloride, ethylaluminumsesquichloride, methylaluminumsesquichloride, and alumoxanes. Alumoxanes are well known in the art as typically the oligomeric compounds which can be prepared by the controlled addition of water to an alkylaluminium compound, for example trimethylaluminium. Such compounds can be linear, cyclic or mixtures thereof. Commercially available alumoxanes are generally believed to be mixtures of linear and cyclic compounds. The cyclic alumoxanes can be represented by the formula  $[\text{R}^{16}\text{AlO}]_s$  and the linear alumoxanes by the formula  $\text{R}^{17}(\text{R}^{18}\text{AlO})_s$  wherein s is a number from about 2 to 50, and wherein  $\text{R}^{16}$ ,  $\text{R}^{17}$ , and  $\text{R}^{18}$  represent hydrocarbyl groups, preferably  $\text{C}_1$  to  $\text{C}_6$  alkyl groups, for example methyl, ethyl or butyl groups. Alkylalumoxanes such as methylalumoxane (MAO) are preferred.

Mixtures of alkylalumoxanes and trialkylaluminium compounds are particularly preferred, such as MAO with TMA or TIBA. In this context it should be noted that the term "alkylalumoxane" as used in this specification includes alkylalumoxanes available commercially which may contain a proportion, typically about 10wt%, but optionally up to 50wt%, of the corresponding trialkylaluminium; for instance, commercial MAO usually contains approximately 10wt% trimethylaluminium (TMA), whilst commercial MMAO contains both TMA and TIBA. Quantities of alkylalumoxane quoted herein include such trialkylaluminium impurities, and accordingly quantities of trialkylaluminium compounds quoted herein are considered to comprise compounds of the formula  $\text{AlR}_3$  additional to any  $\text{AlR}_3$  compound incorporated within the alkylalumoxane when present.

Examples of suitable hydrocarbylboron compounds are boroxines, trimethylboron, triethylboron, dimethylphenylammoniumtetra(phenyl)borate, trityltetra(phenyl)borate, triphenylboron, dimethylphenylammonium tetra(pentafluorophenyl)borate, sodium tetrakis[(bis-3,5-trifluoromethyl)phenyl]borate,

$\text{H}^+(\text{OEt}_2)[(\text{bis}-3,5\text{-trifluoromethyl})\text{phenyl}]\text{borate}$ , trityltetra(pentafluorophenyl)borate and tris(pentafluorophenyl) boron.

In the preparation of the catalysts of the present invention the quantity of activating compound selected from organoaluminium compounds and hydrocarbylboron 5 compounds to be employed is easily determined by simple testing, for example, by the preparation of small test samples which can be used to polymerise small quantities of the monomer(s) and thus to determine the activity of the produced catalyst. It is generally found that the quantity employed is sufficient to provide 0.1 to 20,000 atoms, preferably 1 to 2000 atoms of aluminium or boron per atom of metal M in the 10 compound of Formula (I).

An alternative class of activators comprise salts of a cationic oxidising agent and a non-coordinating compatible anion. Examples of cationic oxidising agents include: ferrocenium, hydrocarbyl-substituted ferrocenium,  $\text{Ag}^+$ , or  $\text{Pb}^{2+}$ . Examples of non-coordinating compatible anions are  $\text{BF}_4^-$ ,  $\text{SbCl}_6^-$ ,  $\text{PF}_6^-$ , tetrakis(phenyl)borate and 15 tetrakis(pentafluorophenyl)borate.

The polymerisation catalyst of the present invention may also comprise (3) a neutral Lewis base.

Neutral Lewis bases are well known in the art of Ziegler-Natta catalyst polymerisation technology. Examples of classes of neutral Lewis bases suitably 20 employed in the present invention are unsaturated hydrocarbons, for example, alkenes (other than 1-olefins) or alkynes, primary, secondary and tertiary amines, amides, phosphoramides, phosphines, phosphites, ethers, thioethers, nitriles, carbonyl compounds, for example, esters, ketones, aldehydes, carbon monoxide and carbon dioxide, sulphoxides, sulphones and boroxines. Although 1-olefins are capable of 25 acting as neutral Lewis bases, for the purposes of the present invention they are regarded as monomer or comonomer 1-olefins and not as neutral Lewis bases *per se*. However, alkenes which are internal olefins, for example, 2-butene and cyclohexene are regarded as neutral Lewis bases in the present invention. Preferred Lewis bases are tertiary amines and aromatic esters, for example, dimethylaniline, diethylaniline, 30 tributylamine, ethylbenzoate and benzylbenzoate. In this particular aspect of the present invention, components (1), (2) and (3) of the catalyst system can be brought together simultaneously or in any desired order. However, if components (2) and (3)

are compounds which interact together strongly, for example, form a stable compound together, it is preferred to bring together either components (1) and (2) or components (1) and (3) in an initial step before introducing the final defined component. Preferably components (1) and (3) are contacted together before 5 component (2) is introduced. The quantities of components (1) and (2) employed in the preparation of this catalyst system are suitably as described above in relation to the catalysts of the present invention. The quantity of the neutral Lewis Base [component (3)] is preferably such as to provide a ratio of component (1):component (3) in the range 100:1 to 1:1000, most preferably in the range 1:1 to 1:20. Components (1), (2) and (3) 10 of the catalyst system can brought together, for example, as the neat materials, as a suspension or solution of the materials in a suitable diluent or solvent (for example a liquid hydrocarbon), or, if at least one of the components is volatile, by utilising the vapour of that component. The components can be brought together at any desired temperature. Mixing the components together at room temperature is generally 15 satisfactory. Heating to higher temperatures e.g. up to 120°C can be carried out if desired, e.g. to achieve better mixing of the components. It is preferred to carry out the bringing together of components (1), (2) and (3) in an inert atmosphere (e.g. dry nitrogen) or *in vacuo*. If it is desired to use the catalyst on a support material (see below), this can be achieved, for example, by performing the catalyst system 20 comprising components (1), (2) and (3) and impregnating the support material preferably with a solution thereof, or by introducing to the support material one or more of the components simultaneously or sequentially. If desired the support material itself can have the properties of a neutral Lewis base and can be employed as, or in place of, component (3). An example of a support material having neutral Lewis base properties 25 is poly(aminostyrene) or a copolymer of styrene and aminostyrene (ie vinylaniline).

The catalysts of the present invention can if desired comprise more than one of the defined compounds. Alternatively, the catalysts of the present invention can also include one or more other types of transition metal compounds or catalysts, for example, nitrogen containing catalysts such as those described in WO 99/12981. 30 Examples of such other catalysts include 2,6-diacetylpyridinebis(2,4,6-trimethyl anil)FeCl<sub>2</sub>.

The catalysts of the present invention can also include one or more other types of

catalyst, such as those of the type used in conventional Ziegler-Natta catalyst systems, metallocene-based catalysts, monocyclopentadienyl- or constrained geometry based catalysts, or heat activated supported chromium oxide catalysts (eg Phillips-type catalyst).

5 The catalysts of the present invention can be unsupported or supported on a support material, for example, silica, alumina, MgCl<sub>2</sub> or zirconia, or on a polymer or prepolymer, for example polyethylene, polypropylene, polystyrene, or poly(aminostyrene).

If desired the catalysts can be formed in situ in the presence of the support  
10 material, or the support material can be pre-impregnated or premixed, simultaneously or sequentially, with one or more of the catalyst components. The catalysts of the present invention can if desired be supported on a heterogeneous catalyst, for example, a magnesium halide supported Ziegler Natta catalyst, a Phillips type (chromium oxide) supported catalyst or a supported metallocene catalyst. Formation of the supported  
15 catalyst can be achieved for example by treating the transition metal compounds of the present invention with alumoxane in a suitable inert diluent, for example a volatile hydrocarbon, slurring a particulate support material with the product and evaporating the volatile diluent. The produced supported catalyst is preferably in the form of a free-flowing powder. The quantity of support material employed can vary widely, for  
20 example from 100,000 to 1 grams per gram of metal present in the transition metal compound.

The present invention further provides a process for the polymerisation and copolymerisation of 1-olefins, comprising contacting the monomeric olefin under polymerisation conditions with the polymerisation catalyst of the present invention. A  
25 preferred process comprises the steps of :

- a) preparing a prepolymer-based catalyst by contacting one or more 1-olefins with a catalyst system, and
- b) contacting the prepolymer-based catalyst with one or more 1-olefins,  
wherein the catalyst system is as defined above.

30 In the text hereinbelow, the term "catalyst" is intended to include "prepolymer-based catalyst" as defined above.

The polymerisation conditions can be, for example, solution phase, slurry phase,

gas phase or bulk phase, with polymerisation temperatures ranging from -100°C to +300°C, and at pressures of atmospheric and above, particularly from 140 to 4100 kPa. If desired, the catalyst can be used to polymerise ethylene under high pressure/high temperature process conditions wherein the polymeric material forms as a melt in supercritical ethylene. Preferably the polymerisation is conducted under gas phase fluidised bed or stirred bed conditions.

Suitable monomers for use in the polymerisation process of the present invention are, for example, ethylene and C<sub>2</sub>-20 α-olefins, specifically propylene, 1-butene, 1-pentene, 1-hexene, 4-methylpentene-1, 1-heptene, 1-octene, 1-nonene, 1-decene, 1-undecene, 1-dodecene, 1-tridecene, 1-tetradecene, 1-pentadecene, 1-hexadecene, 1-heptadecene, 1-octadecene, 1-nonadecene, and 1-eicosene. Other monomers include methyl methacrylate, methyl acrylate, butyl acrylate, acrylonitrile, vinyl acetate, and styrene. Preferred monomers for homopolymerisation processes are ethylene and propylene.

The catalysts and process of the invention can also be used for copolymerising ethylene or propylene with each other or with other 1-olefins such as 1-butene, 1-hexene, 4-methylpentene-1, and octene, or with other monomeric materials, for example, methyl methacrylate, methyl acrylate, butyl acrylate, acrylonitrile, vinyl acetate, and styrene. Polymerisation of 1-olefins with dienes, particularly non-conjugated dienes, such as 1,4 pentadiene, 1,5-hexadiene, cyclopentadiene and ethylene norbornadiene is also possible. In particular, ethylene/1-olefin/diene terpolymers may be made by the process of the invention where the diene is as above and the other 1-olefin is preferably propylene.

Irrespective of the polymerisation or copolymerisation technique employed, polymerisation or copolymerisation is typically carried out under conditions that substantially exclude oxygen, water, and other materials that act as catalyst poisons. Also, polymerisation or copolymerisation can be carried out in the presence of additives to control polymer or copolymer molecular weights.

The use of hydrogen gas as a means of controlling the average molecular weight of the polymer or copolymer applies generally to the polymerisation process of the present invention. For example, hydrogen can be used to reduce the average molecular weight of polymers or copolymers prepared using gas phase, slurry phase, bulk phase or

solution phase polymerisation conditions. The quantity of hydrogen gas to be employed to give the desired average molecular weight can be determined by simple "trial and error" polymerisation tests.

The polymerisation process of the present invention provides polymers and 5 copolymers, especially ethylene polymers, at remarkably high productivity (based on the amount of polymer or copolymer produced per unit weight of complex employed in the catalyst system). This means that relatively very small quantities of transition metal complex are consumed in commercial processes using the process of the present invention. It also means that when the polymerisation process of the present 10 invention is operated under polymer recovery conditions that do not employ a catalyst separation step, thus leaving the catalyst, or residues thereof, in the polymer (e.g. as occurs in most commercial slurry and gas phase polymerisation processes), the amount of transition metal complex in the produced polymer can be very small.

Slurry phase polymerisation conditions or gas phase polymerisation conditions are 15 particularly useful for the production of high or low density grades of polyethylene, and polypropylene. In these processes the polymerisation conditions can be batch, continuous or semi-continuous. Furthermore, one or more reactors may be used, e.g. from two to five reactors in series. Different reaction conditions, such as different temperatures or hydrogen concentrations may be employed in the different reactors. In 20 the slurry phase process and the gas phase process, the catalyst is generally metered and transferred into the polymerisation zone in the form of a particulate solid either as a dry powder (e.g. with an inert gas) or as a slurry. This solid can be, for example, a solid catalyst system formed from the one or more of complexes of the invention and an activator with or without other types of catalysts, or can be the solid catalyst alone with 25 or without other types of catalysts. In the latter situation, the activator can be fed to the polymerisation zone, for example as a solution, separately from or together with the solid catalyst. Preferably the catalyst system or the transition metal complex component of the catalyst system employed in the slurry polymerisation and gas phase polymerisation is supported on one or more support materials. Most preferably the 30 catalyst system is supported on the support material prior to its introduction into the polymerisation zone. Suitable support materials are, for example, silica, alumina, zirconia, talc, kieselguhr, or magnesia. Impregnation of the support material can be

carried out by conventional techniques, for example, by forming a solution or suspension of the catalyst components in a suitable diluent or solvent, and slurring the support material therewith. The support material thus impregnated with catalyst can then be separated from the diluent for example, by filtration or evaporation techniques.

5 Once the polymer product is discharged from the reactor, any associated and absorbed hydrocarbons are substantially removed, or degassed, from the polymer by, for example, pressure let-down or gas purging using fresh or recycled steam, nitrogen or light hydrocarbons (such as ethylene). Recovered gaseous or liquid hydrocarbons may be recycled to the polymerisation zone.

10 In the slurry phase polymerisation process the solid particles of catalyst, or supported catalyst, are fed to a polymerisation zone either as dry powder or as a slurry in the polymerisation diluent. The polymerisation diluent is compatible with the polymer(s) and catalyst(s), and may be an alkane such as hexane, heptane, isobutane, or a mixture of hydrocarbons or paraffins. Preferably the particles are fed to a

15 polymerisation zone as a suspension in the polymerisation diluent. The polymerisation zone can be, for example, an autoclave or similar reaction vessel, or a continuous loop reactor, e.g. of the type well-known in the manufacture of polyethylene by the Phillips Process. When the polymerisation process of the present invention is carried out under slurry conditions the polymerisation is preferably carried out at a temperature above

20 0°C, most preferably above 15°C. The polymerisation temperature is preferably maintained below the temperature at which the polymer commences to soften or sinter in the presence of the polymerisation diluent. If the temperature is allowed to go above the latter temperature, fouling of the reactor can occur. Adjustment of the polymerisation within these defined temperature ranges can provide a useful means of controlling the average molecular weight of the produced polymer. A further useful means of controlling the molecular weight is to conduct the polymerisation in the presence of hydrogen gas which acts as chain transfer agent. Generally, the higher the concentration of hydrogen employed, the lower the average molecular weight of the produced polymer.

25 In bulk polymerisation processes, liquid monomer such as propylene is used as the polymerisation medium.

30 Methods for operating gas phase polymerisation processes are well known in the

art. Such methods generally involve agitating (e.g. by stirring, vibrating or fluidising) a bed of catalyst, or a bed of the target polymer (i.e. polymer having the same or similar physical properties to that which it is desired to make in the polymerisation process) containing a catalyst, and feeding thereto a stream of monomer  
5 at least partially in the gaseous phase, under conditions such that at least part of the monomer polymerises in contact with the catalyst in the bed. The bed is generally cooled by the addition of cool gas (e.g. recycled gaseous monomer) and/or volatile liquid (e.g. a volatile inert hydrocarbon, or gaseous monomer which has been condensed to form a liquid). The polymer produced in, and isolated from, gas phase  
10 processes forms directly a solid in the polymerisation zone and is free from, or substantially free from liquid. As is well known to those skilled in the art, if any liquid is allowed to enter the polymerisation zone of a gas phase polymerisation process the quantity of liquid in the polymerisation zone is small in relation to the quantity of polymer present.. This is in contrast to "solution phase" processes wherein the polymer  
15 is formed dissolved in a solvent, and "slurry phase" processes wherein the polymer forms as a suspension in a liquid diluent.

The gas phase process can be operated under batch, semi-batch, or so-called "continuous" conditions. It is preferred to operate under conditions such that monomer is continuously recycled to an agitated polymerisation zone containing polymerisation  
20 catalyst, make-up monomer being provided to replace polymerised monomer, and continuously or intermittently withdrawing produced polymer from the polymerisation zone at a rate comparable to the rate of formation of the polymer, fresh catalyst being added to the polymerisation zone to replace the catalyst withdrawn from the polymerisation zone with the produced polymer.

25 For typical production of impact copolymers, homopolymer formed from the first monomer in a first reactor is reacted with the second monomer in a second reactor. For manufacture of propylene/ethylene impact copolymer in a gas-phase process, propylene is polymerized in a first reactor; reactive polymer transferred to a second reactor in which ethylene or other comonomer is added. The result is an intimate mixture of a  
30 isotactic polypropylene chains with chains of a random propylene/ethylene copolymer. A random copolymer typically is produced in a single reactor in which a minor amount of a comonomer (typically ethylene) is added to polymerizing chains of propylene.

Methods for operating gas phase fluidised bed processes for making polyethylene, ethylene copolymers and polypropylene are well known in the art. The process can be operated, for example, in a vertical cylindrical reactor equipped with a perforated distribution plate to support the bed and to distribute the incoming fluidising gas stream

5 through the bed. The fluidising gas circulating through the bed serves to remove the heat of polymerisation from the bed and to supply monomer for polymerisation in the bed. Thus the fluidising gas generally comprises the monomer(s) normally together with some inert gas (e.g. nitrogen or inert hydrocarbons such as methane, ethane, propane, butane, pentane or hexane) and optionally with hydrogen as molecular weight

10 modifier. The hot fluidising gas emerging from the top of the bed is led optionally through a velocity reduction zone (this can be a cylindrical portion of the reactor having a wider diameter) and, if desired, a cyclone and or filters to disentrain fine solid particles from the gas stream. The hot gas is then led to a heat exchanger to remove at least part of the heat of polymerisation. Catalyst is preferably fed continuously or at

15 regular intervals to the bed. At start up of the process, the bed comprises fluidisable polymer which is preferably similar to the target polymer. Polymer is produced continuously within the bed by the polymerisation of the monomer(s). Preferably means are provided to discharge polymer from the bed continuously or at regular intervals to maintain the fluidised bed at the desired height. The process is generally

20 operated at relatively low pressure, for example, at 10 to 50 bars, and at temperatures for example, between 50 and 120 °C. The temperature of the bed is maintained below the sintering temperature of the fluidised polymer to avoid problems of agglomeration.

In the gas phase fluidised bed process for polymerisation of olefins the heat evolved by the exothermic polymerisation reaction is normally removed from the

25 polymerisation zone (i.e. the fluidised bed) by means of the fluidising gas stream as described above. The hot reactor gas emerging from the top of the bed is led through one or more heat exchangers wherein the gas is cooled. The cooled reactor gas, together with any make-up gas, is then recycled to the base of the bed. In the gas phase fluidised bed polymerisation process of the present invention it is desirable to provide

30 additional cooling of the bed (and thereby improve the space time yield of the process) by feeding a volatile liquid to the bed under conditions such that the liquid evaporates in the bed thereby absorbing additional heat of polymerisation from the bed by the "latent

heat of evaporation" effect. When the hot recycle gas from the bed enters the heat exchanger, the volatile liquid can condense out. In one embodiment of the present invention the volatile liquid is separated from the recycle gas and reintroduced separately into the bed. Thus, for example, the volatile liquid can be separated and 5 sprayed into the bed. In another embodiment of the present invention the volatile liquid is recycled to the bed with the recycle gas. Thus the volatile liquid can be condensed from the fluidising gas stream emerging from the reactor and can be recycled to the bed with recycle gas, or can be separated from the recycle gas and then returned to the bed.

The method of condensing liquid in the recycle gas stream and returning the 10 mixture of gas and entrained liquid to the bed is described in EP-A-0089691 and EP-A-0241947. It is preferred to reintroduce the condensed liquid into the bed separate from the recycle gas using the process described in our US Patent 5541270, the teaching of which is hereby incorporated into this specification.

When using the catalysts of the present invention under gas phase polymerisation 15 conditions, the catalyst, or one or more of the components employed to form the catalyst can, for example, be introduced into the polymerisation reaction zone in liquid form, for example, as a solution in an inert liquid diluent. Thus, for example, the transition metal component, or the activator component, or both of these components can be dissolved or slurried in a liquid diluent and fed to the polymerisation zone. 20 Under these circumstances it is preferred the liquid containing the component(s) is sprayed as fine droplets into the polymerisation zone. The droplet diameter is preferably within the range 1 to 1000 microns. EP-A-0593083, the teaching of which is hereby incorporated into this specification, discloses a process for introducing a polymerisation catalyst into a gas phase polymerisation. The methods disclosed in EP- 25 A-0593083 can be suitably employed in the polymerisation process of the present invention if desired.

Although not usually required, upon completion of polymerisation or copolymerisation, or when it is desired to terminate polymerisation or copolymerisation or at least temporarily deactivate the catalyst or catalyst component of this invention, 30 the catalyst can be contacted with water, alcohols, acetone, or other suitable catalyst deactivators a manner known to persons of skill in the art.

Homopolymerisation of ethylene with the catalysts of the invention may produce

so-called "high density" grades of polyethylene. These polymers have relatively high stiffness and are useful for making articles where inherent rigidity is required. Copolymerisation of ethylene with higher 1-olefins (e.g. butene, hexene or octene) can provide a wide variety of copolymers differing in density and in other important physical properties. Particularly important copolymers made by copolymerising ethylene with higher 1-olefins with the catalysts of the invention are the copolymers having a density in the range of 0.91 to 0.93. These copolymers which are generally referred to in the art as linear low density polyethylene, are in many respects similar to the so called low density polyethylene produced by the high pressure free radical catalysed polymerisation of ethylene. Such polymers and copolymers are used extensively in the manufacture of flexible blown film.

Propylene polymers produced by the process of the invention include propylene homopolymer and copolymers of propylene with less than 50 mole % ethylene or other alpha-olefin such as butene-1, pentene-1, 4-methylpentene-1, or hexene-1, or mixtures thereof. Propylene polymers also may include copolymers of propylene with minor amounts of a copolymerizable monomer. Typically, most useful are normally-solid polymers of propylene containing polypropylene crystallinity, random copolymers of propylene with up to about 10 wt.% ethylene, and impact copolymers containing up to about 20 wt.% ethylene or other alpha-olefin. Polypropylene homopolymers may contain a small amount (typically below 2 wt.%) of other monomers to the extent the properties of the homopolymer are not affected significantly.

Propylene polymers may be produced which are normally solid, predominantly isotactic, poly  $\alpha$ -olefins. Levels of stereorandom by-products are sufficiently low so that useful products can be obtained without separation thereof. Typically, useful propylene homopolymers show polypropylene crystallinity and have isotactic indices above 90 and many times above 95. Copolymers typically will have lower isotactic indices, typically above 80-85.

Depending upon polymerisation conditions known in the art, propylene polymers with melt flow rates from below 1 to above 1000 may be produced in a reactor. For many applications, polypropylenes with a MFR from 2 to 100 are typical. Some uses such as for spunbonding may use a polymer with an MFR of 500 to 2000.

Depending upon the use of the polymer product, minor amounts of additives are

typically incorporated into the polymer formulation such as acid scavengers, antioxidants, stabilizers, and the like. Generally, these additives are incorporated at levels of about 25 to 2000 ppm, typically from about 50 to about 1000 ppm, and more typically 400 to 1000 ppm, based on the polymer.

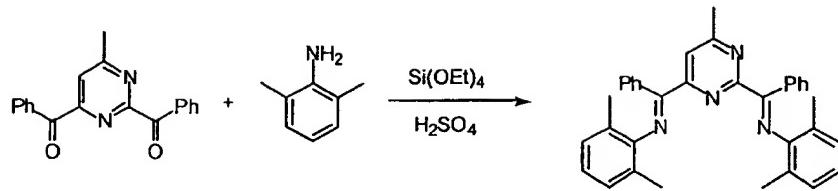
- 5 In use, polymers or copolymers made according to the invention in the form of a powder are conventionally compounded into pellets. Examples of uses for polymer compositions made according to the invention include use to form fibres, extruded films, tapes, spunbonded webs, moulded or thermoformed products, and the like. The polymers may be blown into films, or may be used for making a variety of moulded or  
10 extruded articles such as pipes, and containers such as bottles or drums. Specific additive packages for each application may be selected as known in the art. Examples of supplemental additives include slip agents, anti-blocks, anti-stats, mould release agents, primary and secondary anti-oxidants, clarifiers, nucleants, uv stabilizers, and the like. Classes of additives are well known in the art and include phosphite antioxidants,  
15 hydroxylamine (such as N,N-dialkyl hydroxylamine) and amine oxide (such as dialkyl methyl amine oxide) antioxidants, hindered amine light (uv) stabilizers, phenolic stabilizers, benzofuranone stabilizers, and the like. Various olefin polymer additives are described in U.S. patents 4,318,845, 4,325,863, 4,590,231, 4,668,721, 4,876,300, 5,175,312, 5,276,076, 5,326,802, 5,344,860, 5,596,033, and 5,625,090.  
20 Fillers such as silica, glass fibers, talc, and the like, nucleating agents, and colourants also may be added to the polymer compositions as known by the art.

The present invention is illustrated in the following Examples.

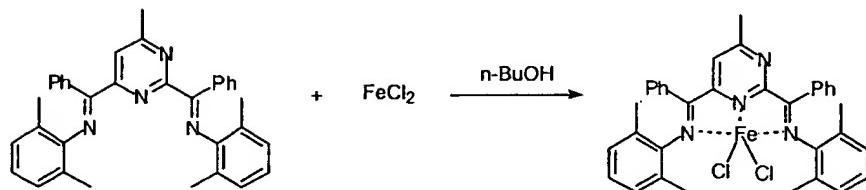
All manipulations were carried out under an atmosphere of nitrogen. Solvents were refluxed over an appropriate drying agent, and distilled prior to use.

25

Synthetic route to  $\alpha$ -amino carbon substituted pyrimidyl(bis)imino iron(II) chloride procatalysts



Synthesis of pyrimidyl(bis)imine ligand 1



Scheme 1.2

Synthesis of pyrimidyl(bis)imino iron(II) chloride procatalysts 2

EXAMPLE 1 - Synthesis of 2,4-{[N-(2,6-dimethylphenyl)]phenylimidoyl}6-methyl pyrimidine ligand 1

5        2,4-dibenzoyl-6-methylpyrimidine (prepared a described in Yamamoto, Y; Ouchi, H; Tanaka, T.; Morita, Y. *Heterocycles* 1995, 41, 1275) (262mg, 0.86 mmol) and aniline (230mg, 1.90mmol) were combined and treated with one drop of concentrated H<sub>2</sub>SO<sub>4</sub> according to the procedure described in Love B.E; Ren. J.; *J. Org. Chem.* 1993, 58, 5556. The Si(OEt)<sub>4</sub> (398mg, 1.90 mmol) was added and the mixture was placed in a flask equipped with a still head. The solution was heated at 150°C under nitrogen for 5h. The distillate (EtOH) was discarded and the residue was dissolved in dichloromethane and washed with saturated NaHCO<sub>3</sub>. The organic phase was dried over MgSO<sub>4</sub> and solvent was removed under reduced pressure. The crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate: 8/2) followed by recrystallisation in ether. Multi isomeric compound. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): 1.62 (s, 3H), 2.08 (s, 3H), 2.33 (s, 3H), 6.80-7.00 (m, 6H), 7.15-7.25 (m, 7H), 7.60-7.80 (m, 4H). MS (EI) *m/z* 508 (100%, M+), 208 (78%, M-Ph-C=N-C<sub>6</sub>H<sub>3</sub>(CH<sub>3</sub>)<sub>2</sub>).

10

15

EXAMPLE 2 - Synthesis of 2,4-{[N-(2,6-dimethylphenyl)]phenylimidoyl}6-methyl pyrimidine iron (II) dichloride procatalyst 2

To a solution of anhydrous FeCl<sub>2</sub> in 10ml of hot n-butanol (80°C) was added ligand 1 (in one portion). The mixture was stirred overnight to produce a dark green precipitate. The solvent was then removed, the solid washed with diethyl ether (3x20ml) and then dried to yield procatalyst 2 as a green solid (60mg). 62%. MS (FAB) *m/z*, 634 (M)+, 599 (M-Cl)+, 564 (M-2Cl)+, 509 (M-2Cl-L).

EXAMPLE 3 - Polymerisation of ethylene

General conditions: In a flame dried Schlenk tube, a solution of procatalyst 2 (7.0mg, 11 mol) in degassed toluene (100ml) was treated with MAO (0.75ml, 1.1mmol, 100 eq.). Colour changed from green to purple. The Schlenk was flushed with ethylene at 1 bar pressure and the solution was stirred at room temperature over a period of 1 hour. The reaction was quenched with diluted HCl, the solid PE precipitated in methanol and dried in vacuum at 50°C for 4 hours. Polymer yield = 23.4 grams, equivalent to 2130 gPE/mmol.hr.bar.

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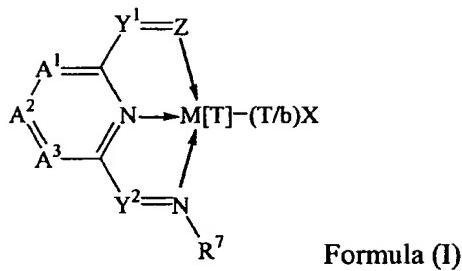
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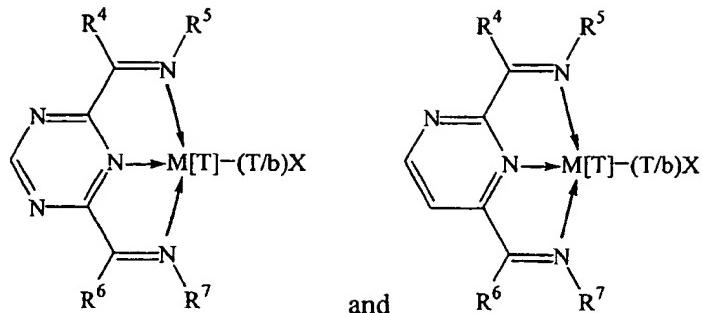
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## CLAIMS

## 1. Complex having the Formula (I)

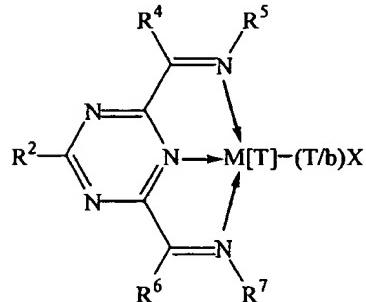


wherein M is a transition metal; X represents an atom or group covalently or ionically  
 5 bonded to M; T is the oxidation state of M; b is the valency of the atom or group X; A<sup>1</sup>  
 to A<sup>3</sup> are each independently N or P or CR, with the proviso that at least one but no  
 more than two of them are independently CR; Y<sup>1</sup> and Y<sup>2</sup> are each independently CR' or  
 PR'R''; Z is oxygen or NR<sup>5</sup>; R<sup>5</sup> and R<sup>7</sup> and each R, each R' and each R'' are  
 independently selected from hydrogen, halogen, hydrocarbyl, substituted hydrocarbyl,  
 10 heterohydrocarbyl, substituted heterohydrocarbyl or SiR<sup>30</sup><sub>3</sub> where each R<sup>30</sup> is  
 independently selected from hydrogen, halogen, hydrocarbyl, substituted hydrocarbyl,  
 heterohydrocarbyl and substituted heterohydrocarbyl;  
 but excluding those complexes having the formulae

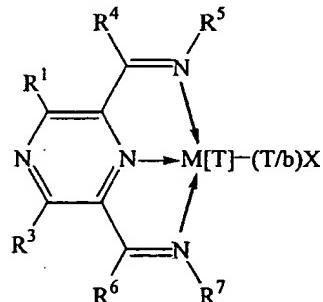


where in both cases  $R^4$  and  $R^6$  are Me,  $R^5$  and  $R^7$  are 2,4,6-trimethylphenyl, M is Fe, T is II, X is Cl and b is 1.

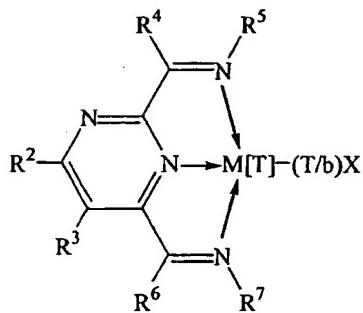
- 5    2. Complex according to claim 1, wherein the metal M is iron, cobalt, vanadium, titanium, ruthenium, hafnium, manganese, zirconium, rhodium or iridium.
- 3. Complex according to claim 1 or 2, wherein  $A^1$  to  $A^3$  are each independently N or CR, subject to the proviso of claim 1.
- 4. Complex according to claim 3, wherein either: one or both of  $A^1$  and  $A^3$  are N; or
- 10   A<sup>2</sup> alone is N.
- 5. Complex according to any preceding claim, wherein Y<sup>1</sup> is CR<sup>4</sup> and Y<sup>2</sup> is CR<sup>6</sup>.
- 6. Complex according to claim 5, wherein R<sup>4</sup> and R<sup>6</sup> are ethyl, isopropyl, t-butyl, phenyl or CH<sub>2</sub>CH<sub>2</sub>Ph.
- 7. Complex according to any preceding claim, wherein Z is NR<sup>5</sup>.
- 15   8. Complex according to any preceding claim, comprising one of the following:



Formula (IIa)

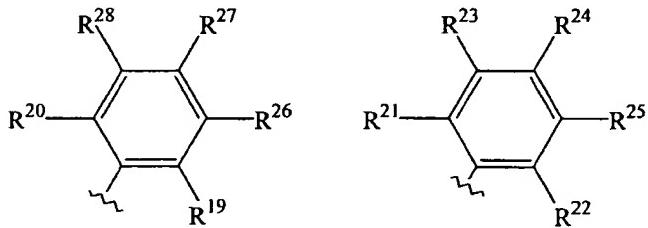


Formula (IIb)



**Formula to (IIc)**

- wherein R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> are each independently H, or C<sub>1</sub>-C<sub>10</sub> alkyl, aryl or arylalkyl, and  
5 the other substituents are as defined in the preceding claims, subject to the proviso of  
claim 1.
9. Complex according to claim 8, wherein R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> are each independently H or  
C<sub>1</sub>-C<sub>10</sub> alkyl, preferably each independently H, methyl or ethyl.
10. Complex according to any one of claims 7 to 9, wherein R<sup>5</sup> is represented by the  
10 group "P" and R<sup>7</sup> is represented by the group "Q" as follows:



Group P

Group Q

- wherein R<sup>19</sup> to R<sup>28</sup> are independently selected from hydrogen, halogen, hydrocarbyl,  
15 substituted hydrocarbyl, heterohydrocarbyl or substituted heterohydrocarbyl; when any  
two or more of R<sup>1</sup> to R<sup>4</sup>, R<sup>6</sup> and R<sup>19</sup> to R<sup>28</sup> are hydrocarbyl, substituted hydrocarbyl,  
heterohydrocarbyl or substituted heterohydrocarbyl, said two or more can be linked to  
form one or more cyclic substituents.

11. Complex according to claim 10, wherein the ring systems P and Q are each  
20 independently phenyl, 2-methylphenyl, 2-ethylphenyl, 2,6-diisopropylphenyl,  
2,3-diisopropylphenyl, 2,4-diisopropylphenyl, 2,6-di-n-butylphenyl, 2,6-  
dimethylphenyl, 2,3-dimethylphenyl, 2,4-dimethylphenyl, 2-t-butylphenyl, 2,6-

- diphenylphenyl, 2,4,6-trimethylphenyl, 2,6-trifluoromethylphenyl, 4-bromo-2,6-dimethylphenyl, 3,5-dichloro2,6-diethylphenyl, or 2,6-bis(2,6-dimethylphenyl)phenyl.
12. Complex according to any preceding claim, wherein X is chloride, bromide; hydride; methoxide, ethoxide, isopropoxide, phenoxide; formate, acetate, benzoate; 5 methyl, ethyl, propyl, butyl, octyl, decyl, phenyl, benzyl; substituted hydrocarbyl; heterohydrocarbyl; tosylate; or triflate.
13. Complex according to any preceding claim, which is one of the following:
- 2,4-{[N-(2,6-dimethylphenyl)]phenylimidoyl}6-methyl pyrimidine iron (II) dichloride  
2,4-{[N-(2,4,6-trimethylphenyl)]phenylimidoyl}6-methyl pyrimidine iron (II)  
10 dichloride  
2,4-{[N-(2,6-dimethyl-4-*tert*butylphenyl)]phenylimidoyl}6-methyl pyrimidine iron (II) dichloride  
2,4-{[N-(2-methylphenyl)]phenylimidoyl}6-methyl pyrimidine iron (II) dichloride  
2,4-{[N-(1,1-diphenylamino)]phenylimidoyl}6-methyl pyrimidine iron (II) dichloride  
15 2,6-{[N-(2,6-dimethylphenyl)]phenylimidoyl} pyrazine iron (II) dichloride  
2,6-{[N-(2,4,6-trimethylphenyl)]phenylimidoyl} pyrazine iron (II) dichloride  
2,6-{[N-(2,6-dimethyl-4-*tert*butylphenyl)]phenylimidoyl} pyrazine iron (II) dichloride  
2,6-{[N-(2-methylphenyl)]phenylimidoyl} pyrazine iron (II) dichloride.
14. Polymerisation catalyst comprising
- 20 (1) a complex as defined in any preceding claim, and  
(2) an activating quantity of at least one activator compound.
15. Catalyst according to claim 14 wherein the activator is selected from organoaluminium compounds, hydrocarbylboron compounds and salts of a cationic oxidising agent and a non-coordinating compatible anion..
- 25 16. Catalyst according to claim 15 wherein the activator is selected from trimethylaluminium (TMA), triethylaluminium (TEA), tri-isobutylaluminium (TIBA), tri-n-octylaluminium, methylaluminium dichloride, ethylaluminium dichloride, dimethylaluminium chloride, diethylaluminium chloride, ethylaluminumsesquichloride, methylaluminumsesquichloride, and alumoxanes.
- 30 17. Catalyst according to any one of claims 14 to 16, further comprising a neutral Lewis base.
18. Catalyst according to claim 17 wherein the neutral Lewis base is selected from

alkenes (other than 1-olefins) or alkynes, primary, secondary and tertiary amines, amides, phosphoramides, phosphines, phosphites, ethers, thioethers, nitriles, esters, ketones, aldehydes, carbon monoxide and carbon dioxide, sulphoxides, sulphones and boroxines.

- 5    19. Catalyst according to any one of claims 14 to 18 which is supported on a support material comprising silica, alumina, MgCl<sub>2</sub> or zirconia, or on a polymer or prepolymer comprising polyethylene, polypropylene, polystyrene, or poly(aminostyrene).
- 10    20. Catalyst according to any one of claims 14 to 18 which comprises more than one complex as defined in any of claims 1 to 13, or a complex as defined in any of claims 1 to 13 plus a further tridentate nitrogen-containing Fe or Co complex, which is preferably 6-diacetylpyridinebis(2,4,6-trimethyl anil)FeCl<sub>2</sub>.
- 15    21. Catalyst according to any one of claims 14 to 19 which comprises a complex as defined in any of claims 1 to 13 plus a further catalyst suitable for the polymerisation of 1-olefins, preferably a Ziegler-Natta catalyst system, metallocene-based catalyst, monocyclopentadienyl- or constrained geometry based catalyst, or heat activated supported chromium oxide catalyst.
- 20    22. Process for the polymerisation or copolymerisation of 1-olefins, comprising contacting a monomeric olefin under polymerisation conditions with a complex or catalyst as defined in any preceding claim.
- 25    23. Process according to claim 22 comprising the steps of :
  - a) preparing a prepolymer-based catalyst by contacting one or more 1-olefins with a catalyst, and
  - b) contacting the prepolymer-based catalyst with one or more 1-olefins, wherein the catalyst is as defined in any of claims 14 to 21.
- 30    24. Process according to claim 22 or 23 wherein the polymerisation is conducted in the presence of hydrogen as a molecular weight modifier.
- 25    25. Process according to any one of claims 22 to 24 wherein the polymerisation conditions are solution phase, slurry phase or gas phase.
- 26    26. Process according to claim 25 wherein the polymerisation is conducted under gas phase fluidised bed conditions.
- 27    27. Process according to claim 25 wherein the polymerisation is conducted in slurry phase in an autoclave or continuous loop reactor.

28. Use of a complex as defined in any of claims 1 to 13 as a catalyst for the polymerisation of 1-olefins.

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# INTERNATIONAL SEARCH REPORT

Inte. .onal Application No

PCT/GB 01/00249

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC 7 C08F10/00 C08F4/70 C07F15/02

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08F C07F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

CHEM ABS Data, EPO-Internal, WPI Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 924 223 A (MITSUI CHEMICALS INC) 23 June 1999 (1999-06-23) cited in the application page 125 example 28	1-28
A	SEDNEY, DIANA ET AL: "Characterization of the thermolysis products of Fe(TPTZ)2C12.cndot.nH2O and the related 2,4,6-tris(2-pyridyl)-1,3,5-triazine complexes Zn(TPTZ)C12 and Fe(TPTZ)C13" INORG. CHEM. (1981), 20(10), 3476-81 , XP000990130 page 3476 page 3477; example 1	1-28 -/-



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

\* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"g" document member of the same patent family

Date of the actual completion of the international search

16 March 2001

Date of mailing of the international search report

03.05.2001

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Parry, J

**INTERNATIONAL SEARCH REPORT**International Application No  
PCT/GB 01/00249**C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT**

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 99 50318 A (CITRON JOEL DAVID ;COUGHLIN EDWARD BRYAN (US); DU PONT (US); WANG) 7 October 1999 (1999-10-07) examples 1-11 page 24 -page 25 _____	1-28

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/GB 01/00249

### Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1.  Claims Nos.: because they relate to subject matter not required to be searched by this Authority, namely:
2.  Claims Nos.: 1-28 (in part)  
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:  
see FURTHER INFORMATION sheet PCT/ISA/210
3.  Claims Nos.: because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

### Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1.  As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2.  As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3.  As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4.  No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

#### Remark on Protest

- The additional search fees were accompanied by the applicant's protest.  
 No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: 1-28 (in part)

Present claims 1-28 relate to an extremely large number of possible compounds and methods. Support within the meaning of Article 6 PCT and/or disclosure within the meaning of Article 5 PCT is to be found, however, for only a very small proportion of the compounds and methods claimed. In the present case, the claims so lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible. Consequently, the search has been carried out for those parts of the claims which appear to be supported and disclosed, namely those parts relating to Formula 1 in claim 1 and the claims depending thereon wherein in Formula 1, A1 must be either N or P, A2 must be CR and A3 must be either N, P or CR and wherein Y1 and Y2 must both be CR'.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International Application No

PCT/GB 01/00249

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP 0924223	A 23-06-1999	JP 2000191713 A SG 74682 A		11-07-2000 22-08-2000
WO 9950318	A 07-10-1999	AU 3454599 A BR 9908406 A EP 1068245 A		18-10-1999 17-10-2000 17-01-2001